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DISSOCIATIVE RECOMBINATION OF INTERSTELLAR IONS: ELECTRONIC STRUCTURE CALCULATIONS FOR HCO^+

W. P. Kraemer
Max-Planck-Institut für Physik und Astrophysik,
Institut für Astrophysik,
Karl-Schwarzchild-Str. 1, 8046 Garching, FRG

and

A. U. Hazi
Lawrence Livermore National Laboratory
University of California
Livermore, CA 94550
USA

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Author's name affiliation

W.P. Kraemer
Max-Planck-Institut für Physik und Astrophysik, Institut fü
Astrophysik, Karl-Schwarzschild-Str. 1, 8046 Garching, FRG

and

A.U. Hazi
Lawrence Livermore National Laboratory
University of California
Livermore, CA 94550, USA

I. INTRODUCTION

In the gas-phase theory of the chemistry in dense interstellar clouds most polyatomic neutral molecules are assumed to be formed by dissociative recombination reactions in which a positive molecular ion captures an electron and dissociates into neutral fragments. The physical process of dissociative recombination was introduced by Bates and Massey [1] to account for the rapid rate of recombination of various molecular ions in the upper atmosphere of the Earth. Since then this reaction has also come to be recognized as an important process in plasmas, lasers, and in interstellar molecular clouds. The subject has been reviewed by several authors [2-8].

The capture of an electron by a positive molecular ion requires that the electron gives up energy when moving from a free to a bound state. This energy may be transferred to a third body or it may be radiated away as a result of a free-bound transition. Three-body encounters become probable only at fairly high concentrations of neutral molecules or electrons, while the radiative process occurs only with small probability and usually leads to very small recombination rates. Especially under the very low density conditions in interstellar molecular clouds the three-body reactions can be rouled out because they are extremely improbable. However, according to the theory of Bates and Massey, the dissociative recombination reaction can be thought of as a process in which the positive molecular ion carries along its own third body to act as an energy removing agent. The process can be described schematically as:

$$AB^+ + e \rightleftharpoons (AB)^{**} \longrightarrow A + B \qquad (1)$$

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where A and B represent atoms or molecular fragments. In the collision of an electron with a molecular ion AB^+ a temporary neutral molecular state AB^{**} is formed. In this initial reaction step the incident electron excites a target electron and itself falls into an unoccupied orbital of the molecule, i.e. the capture of the electron occurs through exchange of energy between the incident and a target electron. The resulting intermediate state AB^{**} is unstable because an electron can be reemitted through autoionization. After electron capture the molecular potential controlling the motion of the nuclei is that of the neutral AB^{**} state rather than that of the initial ion. If this potential happens to be repulsive with respect to one or several dissociation channels, the captured electron can be trapped via dissociation of the intermediate AB^{**} into neutral fragments.

In this picture the dissociative recombination reaction is described as a two-step process consisting of the formation and the dissociation of the intermediate state AB^{**}. There are two features of this process that are not found in atoms. First, the electron capture can take place for electrons of almost any thermal energy. In order that electron capture does occur without transfer of energy between electronic and nuclear motion it is necessary only that at some point on the potential energy surfaces of the ion AB^+ and of the AB^{**} state the vertical difference between the two surfaces be equal to the energy brought in by the incident electron. This point on the potential energy surfaces is called the capture point R_c. The second unique feature of the molecular process is that the dissociation of the intermediate AB^{**} provides an efficient mechanism for trapping the captured electron. The lifetimes of autoionizing states against electron emission are typically of the order of 10^{-14} sec. This time must be compared with the stabilization time, i.e. the time taken by the nuclei to separate along the repulsive AB^{**} potential from the capture point R_c past the so-called stabilization point R_s, the crossover point of the two potentials. From any point on the AB^{**} potential beyond R_s ionization becomes highly improbable assuming the Born-Oppenheimer approximation to be valid. If the potential of AB^{**} intersects the Franck-Condon region of AB^+ the stabilization time is much shorter than the autoionization time and the intermediate state AB^{**} will therefore dissociate rather than reionize by emitting an electron. For electron recombination with atomic ions at moderate densities there is no stabilization mechanism of comparable efficiency. For this reason the recombination rates of molecular ions are normally several orders of magnitude larger than those for atomic ions. The reaction mechanism described above is called the direct process. At medium electron temperatures the dependence of the recombination rate of this direct process on the electron temperature can be derived to be approximately $T^{-1/2}$.

Several earlier experimental studies of the temperature dependence of the recombination rates for a number of reactions indicated however a stronger temperature dependence of about $T^{-3/2}$. This led Bardsley [4] to introduce an alternative three-step reaction mechanism, called the indirect process:

$$AB^{+} + e^{-} \rightleftharpoons (AB)^{*} \rightleftharpoons (AB)^{**} \longrightarrow A + B. \qquad (2)$$

In the first step, a Rydberg state $(AB)^*$ is formed in an excited vibrational level. This involves energy transfer from the incident electron directly to vibrational motions of the nuclei. This initial capture step is followed by predissociation of the Rydberg state. This predissociation can be considered as a two-step process. The step $(AB)^* \rightarrow (AB)^{**}$ arises from configuration interaction between the Rydberg state and the valence state $(AB)^{**}$. If the potential of $(AB)^{**}$ is repulsive (in the region where configuration mixing with $(AB)^*$ is large), recombination will be completed by dissociation.

II. EXPERIMENTAL AND THEORETICAL STUDIES

Dissociative recombination reactions of molecular ions are studied in the laboratory by different experimental techniques such as plasma decay measurements, intersecting beam experiments, and more recently by using the trapped-ion technique. An excellent review of recent experimental work that has been done in this field is given by Mitchell and McGowan [8]. So far experimental studies have focused mainly on the determination of total cross sections or thermal rate coefficients. Experiments are usually performed at medium electron energies and at ion temperatures that are much higher than the very low temperatures characteristic for molecular cloud conditions. Extrapolation of these results to molecular cloud temperatures is not possible. More detailed information (intermediate product state, state of dissociation products) is mostly not available from experiment. In this situation theoretical studies can be rather helpful to supplement experimental information and to gain a better understanding of the reaction mechanism of dissociative recombination reactions.

Experimental studies of dissociative recombination reactions cover a large number of diatomic and polyatomic ions. Many of the molecular ions studied in the laboratory are those that are known from processes in the upper atmosphere of the Earth. With only a few exceptions the rate constants at 300K for diatomic ions are typically of the order $\alpha(300K) \approx (2-4)\times10^{-7}cm^3\ sec^{-1}$. For polyatomic ions the α-values at 300K are usually obtained in the range 2×10^{-7} to $1\times10^{-6}\ cm^3\ sec^{-1}$. Laboratory measurements are also done for cluster ions such as $H_3^+\cdot H_2$, $H3O^+(H_2O)_n$, $NH_4^+\cdot NH_3$, $N_2^+\cdot N_2$, $O_2^+\cdot O_2$, $CO^+\cdot CO$. As an interesting result of these measurements it turns out that the $\alpha(300K)$-values of these clusters are about an order of magnitude larger than those of the unclustered ions. This may have also some implications on the chemistry in molecular clouds.

Recently it has been pointed out by Herbst [9] that no successful experiments have yet been performed to determine the relative amounts of various possible dissociation products. Polyatomic electron-ion dissociative recombination reactions are in fact often quite exoergic for a variety of dissociation channels. In order to obtain branching ratios for various sets of neutral dissociation products Herbst applied the statistical phase-space theory. Calculations were done for a number of interstellar molecular ions such as $HCNH^+$, CH_3^+, NH_4^+, OH_3^+. The general conclusion reached from these calculations is that exoergic polyatomic electron-ion reactions usually do give a variety of different dissociation products. However, the minimal disruption that can occur is found to be usually the major reaction channel.

Although dissociative recombination has been studied in the laboratory since many years, only a few rigorous theoretical studies appeared in the literature so far. This is mainly due to the fact that dissociative recombination cross sections are extremely sensitive to the shape and the relative position of the electronic potentials for the ion AB^+ and the neutral species AB^{**} to each other and that accurate potentials are usually not available for most systems. Existing theoretical work is therefore limited to diatomic ions where the necessary potentials can often be generated from spectroscopic data. Another major problem in theoretical studies arises from the uncertainty about the role of vibrationally excited Rydberg states in the recomination process and from the computational problems in calculating these Rydberg states.

In view of these difficulties, the reaction of H_2^+ ions with electrons is of particular interest because this system offers the best possibility for accurate theoretical calculations to which experimental results can be compared. A problem in comparing experimental results for H_2^+ with theory comes however from the fact that excited vibrational states of the H_2^+ ion are very long lived and that the cross section for H_2^+ recombination depends strongly on the vibrational state of the ion. Despite of the difficulty to produce a plasma with H_2^+ as the dominant ion, several laboratory studies of H_2^+ dissociative recombination were performed recently using the intersecting beams technique [10-14]. Most accurate cross section measurements at energies below 3eV [13] show narrow structures superimposed upon a monotonically decreasing background with an energy dependence close to $E^{-0.9}$. According to McGowan [15] this resonance structure could be a manifestation of the indirect mechanism for dissociative recombination of H_2^+. An alternative explanation of the resonance structure was recently presented by O'Malley [16]. Considering the e-H_2^+ reaction as a direct process, O'Malley's analysis shows that curve crossings of the repulsive H_2^{**} resonance state with various Rydberg states could also give rise to the resonant structure in the dissociative recombination cross section of H_2^+.

The first fully theoretical treatment of the e-H_2^+ collision process was done by Bottcher [17,18] using the projection operator formalism of resonance scattering processes in molecules developed originally by Feshbach [19]. There remained however significant discrepancy between theory and experiment particularly regarding the cross sections at low vibrational energies of the ion and the branching ratios for the formation of different dissociation products. Several theoretical studies were performed since then assuming that at low energies the recombination process proceeds primarily through the lowest doubly excited $(1\sigma_u)^2\ {}^1\Sigma_g^+$

state of H_2 and investigating the importance of Rydberg states for the dissociation step [20-22]. A comprehensive discussion of the large degree of disagreement among various theoretical calculations of the lowest doubly excited ${}^1\Sigma_g{}^+$ state of H_2 is presented in the recent paper by Hazi et al. [23]. In this study the energy and width of the $(1\sigma_u)^2\ {}^1\Sigma_g{}^+$ state of H_2 were calculated using Feshbach projection operators and the Stieltjes moment method. The results of these calculations were used by Giusti et al. [24] to re-investigate the e-$H_2{}^+$ collision process. Calculations were performed for electron energies below 0.5 eV and the lowest three vibrational levels of $H_2{}^+$. It was found that in agreement with experiment [13] Rydberg states lead to narrow structures in the cross sections and that the cross section is very small for the $v = 0$ level of the ion becoming larger however for $v = 1$ and 2. While the overall agreement between the results of these calculations and experiment is reasonable, it appears on the other hand that a quantitative comparison between theory and experiment will only be possible if measurements can be made for single vibrational levels of the $H_2{}^+$ ion.

The actual need for a detailed comparison between experiment and theory becomes evident also in view of the large disagreement between experimental and theoretical results for more complicated systems such as e-NO^+, e-$N_2{}^+$, e-$O_2{}^+$. These diatomic atmospheric ions were studied in the laboratory by various experimental techniques [25-33]. Generally there is good agreement between experimental results obtained with different techniques even though the vibrational populations encountered in the different methods are probably quite different. This indicates that there is only little vibrational state dependence of the total recombination rate coefficients for these diatomic ions which is in apparent contradiction to the vibrational dependence found for rare gas recombination rates [34]. Theoretical studies on NO^+ and $N_2{}^+$ were performed using potential curves that were generated from spectroscopic data. In the case of $N_2{}^+$, the experimental measurements are in total disagreement with the theoretical calculations by Michels [35] who found that the rate coefficients for the $v = 1$ and 2 vibrational states are much smaller than the $v = 0$ value. Subsequent laboratory measurements by Zipf [33] however showed that in fact the $v = 0, 1, 2$ rate coefficients for $N_2{}^+$ are all approximately equal. In the theoretical treatment of the NO^+ ion Lee [36] used experimental data to impose boundary conditions for the various dissociation channels of the reasonance complex. The uncertainty of the theoretical results however is still estimated to be as large as 50%. To study the recombination reaction of $O_2{}^+$ Guberman [37] performed fairly extensive electronic structure calculations of the diabatic potential curves of several excited states of O_2 which are important for electron recombination of $O_2{}^+$ in the lowest five vibrational states. From these calculations Guberman was able to give qualitative explanations for example for the experimental finding by Zipf [33] that the percentage of $O({}^1S)$ formation in the dissociative recombination of $O_2{}^+$ is critically dependent on the initial vibrational state of the ion.

III. ELECTRONIC STRUCTURE CALCULATIONS FOR HCO^+

The present study of the interstellar formyl ion HCO^+ is the first attempt to investigate dissociative recombination for a triatomic molecular ion using an entirely theoretical approach. In the following we will describe a number of fairly extensive electronic structure calculations that were performed to determine the reaction mechanism of the e-HCO^+ process. Similar calculations for the isoelectronic ions HOC^+ and HN_2^+ are in progress.

The ions HCO^+ and HN_2^+ are known to be rather abundant interstellar molecular species playing an important role in the interstellar cloud chemistry. Searches for the isoformyl ion HOC^+ remained unsuccessful for a long time. Only recently HOC^+ was observed in the laboratory [38] and a tentative identification of the ion was made in the source Saggitarius B2, a dense interstellar cloud near the Galactic center [39]. However, the existence of HOC^+ in interstellar clouds still remains to be doubtful and several attempts were made recently to give an explanation for the difficulties of observation of HOC^+ in dense interstellar clouds [39-43].

Under molecular cloud conditions the predominant formation reaction of HCO^+ and HN_2^+ occurs through proton transfer from abundant H_3^+ ions to CO and N_2, respectively. Dissociative recombination with thermal electrons is generally assumed to be the main loss reaction for both ions. Electron recombination rates for HCO^+ were measured in a microwave afterglow/mass spectrometer experiment [44] as $\alpha(HCO^+) = (3.3 \pm 0.5)$ and $(2.0 \pm 0.3)\times 10^{-7}$ cm^3/sec at 205 and 300 K, respectively, leading to a strong temperature dependence ($\sim T^{-1}$) for α. With this temperature dependence a linear extrapolation to the low temperatures in molecular clouds gives α-values in the range of $(3.0-0.6)\times 10^{-6}$ cm^3/sec for cloud temperatures between 20 and 100 K. Current models describing interstellar cloud chemistry use instead a smaller α-value of 2.0×10^{-7} cm^3/sec which is probably a more realistic estimate for the recombination rate of HCO^+ in the lowest vibrational state. Recombination cross sections for HN_2^+ were measured over a wide range of electron energies using a merged electron-ion beam technique [45]. Assuming a Maxwellian distribution of the electron velocities, the rate coefficient for HN_2^+ at 100 K is derived to be as large as $1.5\ 10^{-6}$ cm^3/sec.

There are two major problems with the above experiments. First, the vibrational populations of the initial target ions are not known. Since at the very low temperatures in dense interstellar clouds only the lowest vibrational level of the ions is populated, the interstellar rate coefficients may be quite different from the values extrapolated from measurements at much higher temperatures. Secondly, no information about the electronic states of the dissociation products is available from the experiments. For an understanding of the dissociative recombination reaction mechanism however it is important to know in which electronic states the dissociation products are obtained because this gives information about the resonance state which is formed in the electron capture step.

In the electronic structure calculations the molecular orbitals were approximated by linear combinations of Gaussian-type basis functions located at the nuclear centers. Single-configuration Hartree-Fock self-consistent field (SCF) calculations were performed to optimize the expansion coefficients. The basis set employed here consisted of two groups of basis functions. The first group contains those basis functions that are required to approximate the molecular orbitals of the ion and the neutral resonance state. Functions of this type are used in any electronic structure calculations of molecular valence states. This valence basis was augmented by a second group containing diffuse Gaussian functions that are able to generate a sequence of Rydberg-type orbitals in the molecular orbital basis. These diffuse Rydberg-type orbitals are essential for describing the background continuum of the non-resonant scattering wave function and the series of Rydberg states converging against the ion limit and interacting with the repulsive resonance state.

The valence basis selected for the present calculations consisted of (11s 7p 1d) functions for carbon and oxygen and of (6s 1p) functions for hydrogen, contracted to (5s 4p 1d) and (3s 1p), respectively. This basis set is equivalent to basis sets of triple-zeta plus polarization quality used in other high accuracy electronic structure calculations. In augmenting this valence basis by adding diffuse functions a compromise had to be made because the complexity of the computations increases rapidly with the size of the basis set used. Additional diffuse functions with exponents decreasing in geometrical sequence were therefore distributed in the following way: (7s 5p) functions at the carbon center, (3s 3p) functions at oxygen, and (3s 2p) functions at hydrogen. Maximum flexibility is thus added at the central carbon atom because functions in this location are expected to be most effective. The diffuse functions, while not contributing to the energy of the molecular valence states, are capable to produce a sufficiently large number of diffuse Rydberg-type orbitals. The valence part of the basis set consists of 52 contracted functions whereas the total augmented basis counts as many as 95 functions.

The reliability of the valence basis set was checked by comparing the results of some basic electronic structure calculations with corresponding experimental data. At the simple SCF level of approximation the dissociation energy of $HCO^+(X^1\Sigma^+)$ was obtained as $D_e = 6.16$ eV, which is fairly close to the value of 6.40 eV deduced from most recent proton affinity measurements [46] of CO. This indicates that single-determinant SCF calculations are able to provide a rather good description of the ground electronic state of the HCO^+ ion. Good agreement was further obtained at the SCF level of approximation for the ionization potential of hydrogen: IP(SCF) = 13.60 eV as compared to the true value of 13.6058 eV. The SCF value was calculated as the energy difference between the dissociation limits of HCO and HCO^+ in their ground electronic states. Apart from these results, correlation energy effects are expected to become more important for other energy properties such as ionization potentials of CO and HCO and excitation energies of CO. Using canonical SCF orbitals, single-reference state full single and double excitations CI calculations were performed for the ground electronic states of HCO,

HCO^+, CO^+ and for CO in the ground and the two lowest triplet excited states. Vertical ionization potentials and excitation energies that are deduced from these calculations, are collected in Table 1 and compared with corresponding experimental results. The rather poor agreement between theoretical and experimental results for the ionization potential of HCO (X^2A') is due to the fact that the HCO equilibrium geometry was not fully optimized in the present calculations. At the end of this discussion about the reliability of the basis set, it should also be mentioned that previous accurate theoretical determinations of the rotational and vibrational energy levels of the series of isoelectronic triatomic molecular species such as HCN, HNC, HCO^+, HOC^+, HN_2^+ [47-49] were based on electronic structure calculations employing basis sets that are equivalent to the one used in the present study. These calculations provide very sensitive tests of the correct shapes of the molecular potentials in the minimum region. The average error of the calculated rotational transition frequencies was found to be about 0.5% and that of the vibrational frequencies of the order of a few percent.

TABLE 1:

Energy values (in eV) determining the relative positions of the potentials relevant for dissociative recombination of HCO^+: ionization potentials for H(^{2}S), CO($X^1\Sigma^+$), HCO(X^2A^1), dissociation energy of $HCO^+(X^1\Sigma^+)$, and excitation energy of CO($X^1\Sigma^+$ - a' $^3\Sigma^+$).

	SCF	CI	Exptl.
H(^{2}S) IP	13.60	13.60	13.6058
CO($X^1\Sigma^+$) IP	13.56	13.74	14.0139
$T_e(X^1\Sigma^+$ - a' $^3\Sigma^+)$	-	7.12	6.92
$HCO^+(X\ ^1\Sigma^+)$ D_e	6.16	6.46	6.40
HCO(X^2A^1) IP	9.0	9.2	9.88

The CI calculations on HCO^+ were extended to calculate the entire dissociation potential of $HCO^+(^1\Sigma^+) \rightarrow H^+ + CO(^1\Sigma^+)$. In these calculations the CO distance was held fixed at the equilibrium value in HCO^+, namely at 2.10 a_0, which is close to the equilibrium bond length in carbon monoxide $R_e(CO) = 2.132\ a_0$. The calculations showed that the correlation energy is changing very slowly as a function of the HC separation, which explains the rather good SCF result for the dissociation energy of HCO^+.

Similar CI calculations were also done for the lowest $^2\Sigma^+$ excited state of HCO. The corresponding HC dissociation potential is known to be repulsive with respect to dissociation to $H(^2S) + CO(^1\Sigma^+)$. This HCO state was previously assumed to be possibly responsible for an effective electron recombination reaction of the HCO^+ ion at low temperatures. The calculations proved however that there is no crossing between the HCO $(^2\Sigma^+)$ and $HCO^+(^1\Sigma^+)$ potentials. Variation of the CO distances in both species did not move the two curves closer to each other. According to the present calculations the lowest $^2\Sigma^+$ valence state of HCO does therefore not contribute to direct dissociative recombination of the HCO^+ ion.

By far the most important configuration of HCO^+ in the $^1\Sigma^+$ ground state is the Hartree-Fock configuration (core) $3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4$, where "core" represents the doubly-occupied oxygen and carbon 1s-orbitals. Since the bending potential of HCO^+ was recently calculated to be rather steep [49], it is safe to assume that electron capture by the HCO^+ ion will lead to a linear resonance state, particularly if the process occurs at the low energy conditions in dense interstellar clouds. Existing theoretical studies on HCO [50-53] do not provide sufficiently detailed information on which excited states of HCO could be responsible for the dissociative recombination reaction of the HCO^+ ion. Qualitative considerations based on preliminary calculations of several excited HCO states show that there are essentially two possibilities to form HCO resoncance states in low energy e-HCO^+ collisions.

In the first case, the scattering electron excites a 5σ target electron to a $n\sigma$ orbital $(n > 6)$ and falls itself into the 6σ unoccupied orbital. Particularly for larger n-values the $^2\Sigma^+$ states thus formed belong to a series of Rydberg states converging against the HCO^+ $(^3\Sigma^+)$ ion limit. This excited state of HCO^+ is unstable with respect to the dissociation products $H(^2S) + CO^+(^2\Sigma^+)$. The energy levels at the dissociation limits of this $^3\Sigma^+$ excited state and of the $^1\Sigma^+$ ground state of HCO^+ are separated only by 0.408 eV, i.e. the energy difference between the ionization potentials of carbon monoxide and the hydrogen atom. The location of the Rydberg states relative to the ionization limit were obtained using the simple formula

$$E_n^{Ryd}(R) = E^{Ion}(R) - \frac{0.5}{(n-\delta)^2} \qquad (3)$$

where n is the primary quantum number and δ the quantum defect. It turns out that the lowest repulsive Rydberg states cross the ion potential in an energy region that is much too high to be accessible under interstellar cloud conditions.

The other possibility to form an HCO resonance state in low energy e-HCO^+ collisions is that the energy transfer from the scattering electron leads to a $\pi\pi^*$ -excitation of a target electron while the captured electron ends up in the 6σ unoccupied orbital. The $^2\Sigma^+$ state thus formed may be described as a combination of a hydrogen with the $\pi\pi^*$ states of CO. The electronic configuration of this state is essentially $(1\text{-}4\sigma)^2$

$5\sigma^2 6\sigma 1\sigma^3 2\pi$. For large HC separations the 6σ orbital becomes a hydrogen 1s orbital and the dissociation products of the lowest lying member of these states are $H(^2S) + CO(a'^3\Sigma^+)$. On bending this $^2\Sigma^+$ state goes over into the $B\ ^2A^1$ state that was recently studied by Tanaka and T[illegible]shita [52] and that was assigned as the upper state of one of the hydrocarbon flame bands (A-band). At intermediate HC separations there is a strong configuration mixing of this $^2\Sigma^+$ state with a charge-transfer type configuration $(1\text{-}4\sigma)^2 5\sigma 6\sigma^2 1\pi^4$. This is in agreement with the findings of Tanaka and Davidson [53] in their study of the potential surfaces of the lower electronic states of HCO.

Electronic structure calculations of the dissociation potential of this $^2\Sigma^+$ state were performed. These calculations show that the $^2\Sigma^+$ excited state of HCO discussed here is in fact the lowest possible resonance state crossing the potential of the HCO^+ ion close to its minimum. Dissociation of this HCO state leads to the a' $^3\Sigma^+$ excited state of CO. It should be noticed that the CO bond length of this a' $^3\Sigma^+$ state (R_{CO}=1.359 Å) is considerably larger than that of the $^1\Sigma^+$ ground state of CO (R_{CO} = 1.128 Å) and the CO bond length in HCO^+ (R_{CO} = 1.105 Å). Relaxation of the CO bond length is therefore important in studying the dynamics of the dissociative recombination process of HCO^+.

Summarizing the present electronic structure calculations it appears that there is a sparsity of HCO resonance states that are accessible at low energy e-HCO^+ collisions. In this respect the situation seems to be similar to the one found for the e-H_2^+ reaction.

APPENDIX: METHOD TO CALCULATE ELECTRON CAPTURE WIDTH

Dissociative recombination in a resonant electron scattering process. Computationally the most promising method available at present to deal with such processes is based on the Feshbach formalism [19] and the Stieltjes moment theory [54,55] . The method thus uses projection operator techniques and the golden-rule definition of the resonance width. Square-integrable, L^2, basis functions are employed to describe both the resonant and the non-resonant part of the scattering wave function. Stieltjes moment theory is finally applied to extract a continuous approximation for the width from the discrete representation of the background continuum. For a detailed description of this method covering also various computational applications we refer to recent work by Hazi and co-workers [56-58,23] . In the following we will discuss very briefly a few computational aspects and their implications for the basic electronic structure calculations.

In Feshbach's resonance theory the width of a resonance decaying into an open channel is given by the so-called golden-rule formula

$$\Gamma(E) = 2\pi \left|\langle \Psi_R (H-E) \Psi_E^+ \rangle\right|^2 \tag{4}$$

where Ψ_R describes the resonance state and where $\Psi_E^{\pm}$ is an energy-normalized scattering function representing the non-resonant, background continuum at energy E. The operator H is the full many-electron Hamiltonian. The problem in numerical applications is to determine Ψ_R and $\Psi_E^{\pm}$ in such a form that the above matrix element can be easily evaluated. The resonance state wave function Ψ_R is obtained directly by quantum chemical configuration interaction (CI) procedures. The difficulty arises with the calculation of the nonresonant scattering function $\Psi_E^{\pm}$ because of the non-spherical and non-local nature of the electron-molecule interaction potential. In the Stieltjes moment method this difficulty is avoided by expanding $\Psi_E^{\pm}$ in terms of square-integrable, L^2, many-electron basis functions which are constructed to be orthogonal to the resonance wave function Ψ_R through the use of projection operators.

In the computational method used here, a total function space must first be generated from an orthogonal set of many-electron basis functions (configurations) in such a way that it can be partitioned into a resonant and a non-resonant part from which the wave functions Ψ_R and $\Psi_E^{\pm}$ are obtained. These wave functions are used in a formula analogous to (3) to calculate a discrete spectrum for the width. Apart from the initial generation of the total function space, there are three computational steps in the procedure to determine the resonance width: (i) Construction of projection operators after partitioning of the total function space and calculation of Ψ_R and an approximation to $\Psi_E^{\pm}$ by diagonalizing the full Hamiltonian in the two respective subspaces, (ii) evaluation of the width matrix elements connecting the two subspaces from the golden-rule formula, and (iii) application of Stieltjes moment theory techniques to extract correctly normalized widths from the discrete representation of the background continuum.

In order to be able to generate a suitable set of orthogonal many-electron basis functions defining the total function space, one first has to select an orthogonal one-electron function basis that can accurately describe both the resonance state as well as the target ion plus the scattering electron. The choice of this molecular orbital basis is thus governed by the electronic structure of the ion, the expected nature of the resonance state, and also by the needs to represent the background continuum. The basis must contain two groups of orbitals: those which are required to describe the resonance state and the target ion, and those which can approximate the wave function of the scattering electron. Since both the resonance and the target states are bound states, the molecular orbitals in the first group are those normally used in any electronic structure calculation of ground and low-lying excited states. The second group of orbitals on the other hand must contain numerous diffuse basis functions providing a dense representation particularly of the lower part of the background continuum.

Using this one-electron orbital basis, the total function space $(P_o + Q_o)$ is generated from all those many-electron configurations that are required for an accurate description of the resonance state. It has to be noticed however, that in this total CI space internal consistency between the levels of approximation used for the resonant (Q_o) and the non-resonant (P_o) subspaces is more important than achieving the best possible accuracy for the resonance state itself. The subspace P_o is constructed from those configurations which to first order describe the target ion and the scattered electron. All the remaining configurations are included in the Q_o subspace. The resonance wave function Ψ_R and the corresponding resonance energy ϵ_R are obtained by diagonalizing the transformed Hamiltonian Q_oHQ_o. If P_o contains all the configurations that are essential for describing the target ion, the lowest eigenstate or the few lowest eigenstates of Q_oHQ_o will correspond to the resonance: $\Psi_R = \{\Phi_{Ri}\}$.

After the determination of the resonance function Ψ_R a repartitioning of the function space is performed. This repartioning is found to be essential to incorporate many-electron correlation and polarization effects in the description of the non-resonant continuum. In the case of many-electron target ions such effects must be accounted for if accurate widths are to be obtained. Two new projection operators P and Q are defined as:

$$Q = |\Psi_R\rangle\langle\Psi_R| \tag{5a}$$

and

$$P = 1 - Q = P_o + (Q_o - Q). \tag{5b}$$

The operator P thus contains not only those configurations which approximate the decay channel (originally in subspace P_o) but also the higher, non-resonant solutions of Q_oHQ_o. The discrete representation of the non-resonant continuum is finally obtained by diagonalizing PHP in the basis of all configurations of the total function space. The resulting eigenfunctions $\{X_n\}$ with non-zero eigenvalues ϵ_n form an orthonormal set and they are orthogonal to Ψ_R by construction.

For sufficiently large basis sets each solution X_n approximates Ψ_E^+ with $E = \epsilon_n$ in a region near the nuclei, except for an overall normalization factor. Since the golden-rule formula (4) contains the L^2 function Ψ_R which is localized near the nuclei, the matrix element has no significant contribution from the asymptotic region where X_n fails to approximate $\Psi_E^\pm$ [38,39,40]. It is therefore possible to use the set of functions $\{X_n\}$ to calculate the width matrix elements:

$$\gamma_n = 2\pi|\langle\Psi_R\ H\ X_n\rangle|^2 . \tag{6}$$

However, X_n cannot be used directly to approximate $\Gamma(\epsilon_n)$ because of the different normalization. By analogy to the work on accurate photoionization cross sections by Langhoff and co-workers [54,55], Stieltjes moment theory can be employed to extract appropriately normalized resonance widths from the discrete spectrum obtained from (6).

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